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SOME PROPERTIES OF
SILVER OXIDE FILMS

by

T. L. ROLLINS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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The undersigned certify that they have read,
and recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled Some Properties of Silver
Oxide Films submitted by T. L. Rollins in partial fulfilment
of the requirements for the degree of Master of Science.

ABSTRACT

Thin films of silver oxide were deposited by cathodic sputtering of silver in an oxygen atmosphere on a substrate held at approximately -110°C . The samples obtained were initially of low resistance (10^6 ohms), opaque in the visible region, and nonphotoconducting at room temperature. The material was found to be unstable. Over a period of weeks the resistance steadily increased and at the same time the material became photoconducting. These reproducible changes could be accelerated by heating the samples in air up to 100° . Too high a temperature caused decomposition of the oxide into silver. The energy gap obtained from electrical conductivity measurements and photoconductivity measurements was about 1.4 ev. An impurity level is proposed at about 0.5 ev from the valence band. Final resistance of the samples amounted to about 10^{11} ohms.

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NOTATION

B	- recombination coefficient	μ	- mobility; micron
E_a	- energy at acceptor levels	σ	- electrical conductivity
E_c	- energy at conduction band edge	τ	- response time; lifetime
E_f	- energy at Fermi level		
E_g	- energy gap = $E_c - E_v$		
E_o	- photoconductive threshold energy		
E_v	- energy at valence band edge		
$f(E)$	- Fermi function		
K	- absorption constant		
M	- density of acceptor states		
m_e	- effective electron mass		
m_h	- effective hole mass		
n	- electron density		
N_a	- density of acceptor levels		
N_d	- density of donor levels		
n_d	- density of electrons on donor levels		
$N(E)$	- density of states at energy E		
n_o	- equilibrium density of electrons		
N_v	- density of states in valence band		
p	- hole density		
p_a	- density of holes on acceptor centers		
Q	- rate of generation of photocarriers		
R	- resistance		
R_s	- sample resistance		
$S(E)$	- photosensitivity		

INTRODUCTION

Properties of silver oxide, Ag_2O , have been studied by chemists for almost a century. The reaction



was first shown to be reversible in 1887 by LeChatelier⁽¹⁾.

In 1905-06, G.N. Lewis⁽²⁾ made an extensive study of this reaction. The study of the decomposition of silver oxide has continued to interest chemists, and as recently as 1960 papers on the subject were published by Herley and Prout⁽³⁾ in the United States and by Allen⁽⁴⁾ in Australia. It has only been in the last decade, however, that physicists have taken an active interest in the substance. The reason for the sudden interest is that silver oxide is a semiconductor, and possibly the only structural analogue of the important semiconductor copper oxide, Cu_2O . In 1957 Suzuki⁽⁵⁾ prepared silver oxide by cathodic bombardment of silver in air and studied its decomposition by X-ray diffraction techniques.

Again in 1960 Suzuki⁽⁶⁾ studied the properties and decomposition of silver oxide using X-ray diffraction techniques, this time with chemically prepared samples. In 1961 Gross

and Kreingold⁽⁷⁾ studied the infra-red absorption of silver oxide and compared it to the absorption of copper oxide.

Weichman and Fortin⁽⁸⁾ compared properties of sputtered films and chemically prepared samples in 1964. The purpose of the present work is to study the resistivity, optical absorption,

and photoconductivity of sputtered films of Ag_2O , and from this study to propose a model to guide further investigations.

SAMPLE PREPARATION

The equipment used to prepare the silver oxide samples is shown in figure 1. A silver cathode of radius 3 cm and thickness about 0.5 mm was rolled from 99.999% pure silver and suspended in a bell jar. The bell jar was evacuated and then oxygen was admitted until the pressure was about 0.2 Torr. The oxygen was obtained directly from a high pressure oxygen cylinder. The voltage applied to the cathode could be varied from 0 - 3000 volts using a half-wave rectifier circuit. The substrate was placed directly on the anode.

Substrates used were freshly cleaved sheets of mica, saphire plates, or beryllium oxide plates. Electrical contacts were sputtered platinum or evaporated aluminum, and were deposited on the substrate before the silver oxide was deposited. Samples deposited on the smooth mica or saphire surfaces tended to peel if the sample thickness exceeded about 2μ . Samples up to 10μ thick showed no tendency to peel from the somewhat granular surface of the beryllium oxide plates. Beryllium oxide seemed to be the best substrate of the three for resistivity and photoconductivity measurements, but optical transmission studies required, of course, a transparent substrate. It was found that free films of

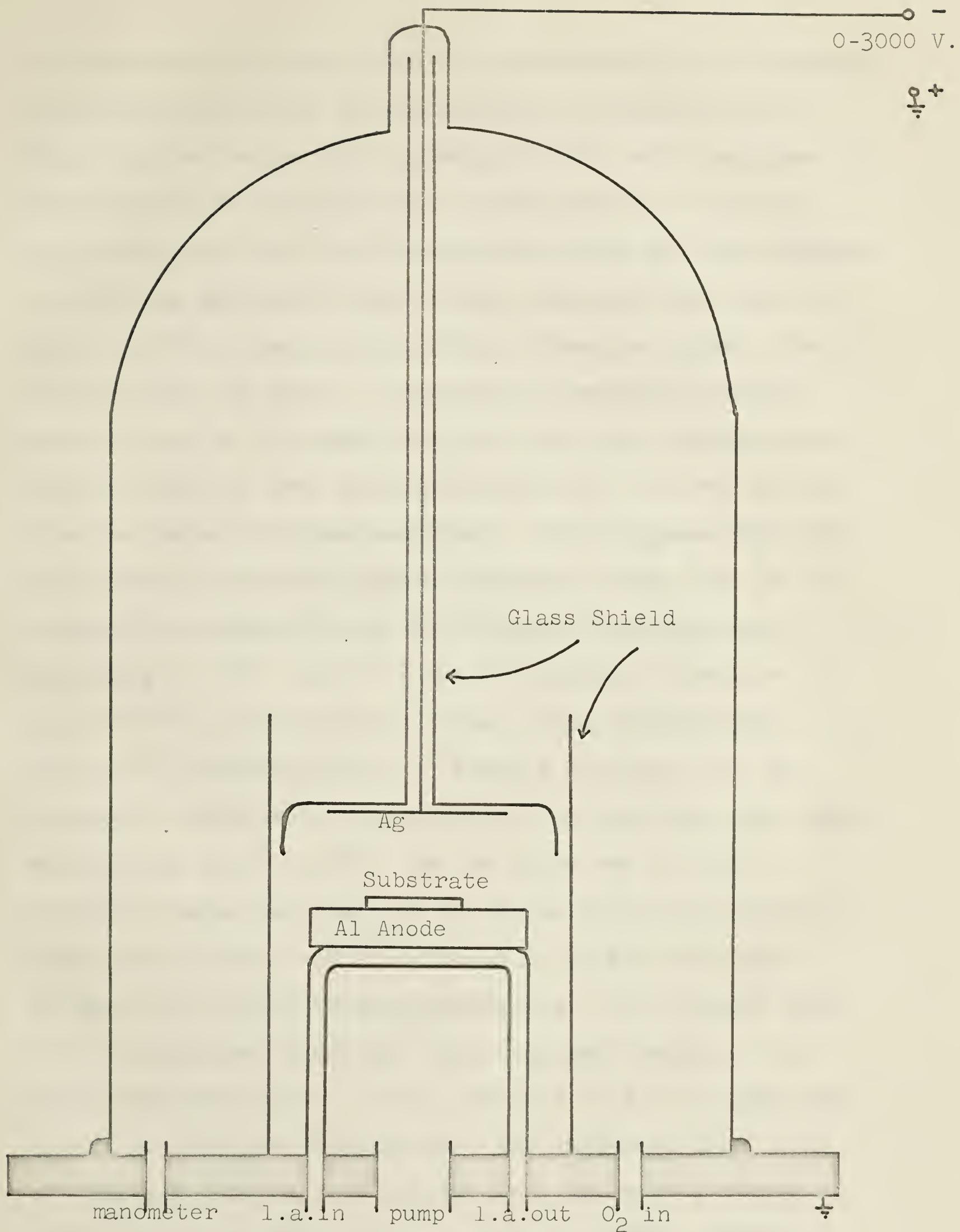


Figure 1 Sputtering Equipment

silver oxide could be obtained by sputtering on to a saphire plate which had first been washed with a soap solution. When a silver oxide film was deposited on such a surface, it could easily be peeled off by blowing gently on the film. Such free films were about one micron thick and very fragile.

During the sputtering process, the anode was held at about -110°C by passing liquid air through a copper tube in contact with the anode. Properties of samples prepared without cooling the anode were scattered and unreproducible. Without cooling, some samples decomposed to silver even before the deposition was completed. Such decomposition probably resulted from the sample becoming hotter than its decomposition temperature at the ambient oxygen pressure.

According to G.N. Lewis⁽²⁾, the decomposition pressure of Ag_2O at 25°C is 0.38 Torr. It was found that results obtained from measurements on samples prepared with the substrate cooled were reproducible. In practice, the anode was held at about -110°C . As the anode was cooled, a definite change was observed in the color of the electrical discharge at about -100°C . The color of the discharge changed from violet to greenish-yellow. At the same time, the voltage across the bell jar increased sharply. The change was reversible. It is possible that the change was caused by some gas freezing onto the anode and thus being effectively removed from the system. It is of interest to note that N_2O and N_2O_3 freeze at about -102°C . Samples

discussed in this paper were prepared at a temperature such that the discharge in the bell jar was greenish-yellow. Unless otherwise noted, samples discussed in this paper were about one micron thick and on a mica substrate.

The values of the voltage and current used for sample preparation were about 1500 volts and 6 ma. Below 1000 volts no deposit was observed, and above about 1800 volts, arcing to the glass walls of the bell jar was observed. The oxygen pressure in the bell jar at 1500 volts and 6 ma was about 0.2 Torr.

According to Holland and Siddall⁽²⁰⁾, some important factors in the sputtering of metal oxide films are:

- (1) Careful control of the oxygen content in the sputtered gas
- (2) The elimination of desorbed gas from the discharge atmosphere
- (3) Temperature control of the cathode and work chamber, etc.
- (4) Control of the purity of the cathode metal.

These factors were not brought to our attention until after our experimental work had been completed, and so our experimental techniques could have been improved. In particular, we should have:

- (1) Determined the purity of the oxygen used.
- (2) Determined the affect of adding various amounts of argon to the sputtering gas. (See Holland and

Siddall, reference 20)

- (3) Eliminated desorbed gases from anode and cathode surfaces by a glow discharge.
- (4) Determined impurities present in silver cathode by spectroscopic analysis.

RESISTIVITY - THEORY

Intrinsic or fully compensated semiconductors: (See Kittel, 17)

An intrinsic semiconductor is one whose electrical properties are not essentially modified by impurities in the crystal. An intrinsic semiconductor is usually one in which the density of electrically active impurities is very low or else one in which the density of donor states is approximately equal to the density of acceptor states. The conductivity σ is given by

$$\sigma = e(n\mu_e + p\mu_h).$$

The first problem then is to calculate n and p . In the intrinsic case $n = p$. The density of electrons in the conduction band is

$$n = \int_{E_c}^{\infty} N(E)f(E)dE$$

where $N(E)$ is the density of available states in the conduction band, given by

$$N(E) = \frac{8\pi m_e}{h^3} (2m_e(E - E_c))^{1/2} / h^3$$

and $f(E)$ is the Fermi function. We will suppose that

$$\exp(E_c - E_f)/kT \gg 1,$$

so that the nondegenerate case results and

$$f(E) = \exp(E_f - E)/kT.$$

$$\text{Then } n = \frac{8\pi m_e}{h^3} (2m_e kT)^{1/2} \exp(E_f - E_c/kT) \int_{E_c}^{\infty} (E - E_c/kT)^{1/2} \exp(E_c - E/kT) dE.$$

Solving, we obtain

$$n = 2(2\pi m_e kT/h^2)^{3/2} \exp(E_f - E_c)/kT.$$

Likewise, we obtain for the hole density in the valence band:

$$p = 2(2\pi m_h kT/h^2) \exp(E_v - E_f/kT).$$

Multiplying together the expressions for n and p we obtain:

$$np = 4(2\pi kT/h^2)^3 (m_e m_h)^{3/2} \exp(-E_g/kT),$$

where $E_g = E_c - E_v$.

Now $np = n^2$, since $n = p$. Therefore,

$$n = 2(2\pi kT/h^2)^{3/2} (m_e m_h)^{3/4} \exp(-E_g/2kT) = p.$$

The conductivity σ is therefore given by

$$\sigma = 2e(2\pi kT/h^2)^{3/2} (m_e m_h)^{3/4} \{\exp(-E_g/2kT)\} \times (\mu_e + \mu_h).$$

As the mobilities are likely to depend on temperature only as a simple power law, the temperature dependence of the conductivity will be dominated by the exponential dependence of the carrier concentration. If we plot $\log R$ vs $1/T$, the slope will be $E_g/2k$.

Extrinsic semiconductor (p type) (See Hannay, reference 16)

Consider a semiconductor with a certain density of acceptor levels N_a all at the same energy, and a smaller density of donor levels N_d , also at one energy. Let p_a be the density of holes on acceptor centers and n_d the density of electrons on donor centers. The densities of holes and electrons in the valence and conduction bands respectively are p and n . The total density of positive charges is then $p + N_d - n_d$, and the total density of negative charges is $n + N_a - p_a$. The condition of charge neutrality requires that $n + N_a - p_a = p + N_d - n_d$. The rate of loss of holes from the acceptor centers to the valence band is

proportional to the number of unionized acceptors ($N_a - N_d - p$) and to the number of empty valence band states (N_v); thus it is given by $K_1 N_v (N_a - N_d - p)$. The rate of return of holes to the acceptor levels is proportional to the number of holes in the valence band (p) and to the number of ionized acceptor states ($p + N_d$), each of which must be counted twice, as there are two possible ways for the hole to enter it, spin up or spin down. This rate, then, is

$$2K_2 p(p + N_d).$$

At equilibrium the rates are equal, so that

$$\frac{2p(p + N_d)}{N_v(N_a - N_d - p)} = \frac{K_1}{K_2} = K \quad (1)$$

where K is the equilibrium constant, a function only of temperature. In the classical approximation it is given by

$$K = \exp(-E_a/kT).$$

We now consider two approximations to equation (1). When $p \gg N_d$, equation (1) reduces to

$$p = (N_v N_a / 2)^{\frac{1}{2}} \exp(-E_a / 2kT). \quad (2)$$

When $p \ll N_d$, equation (1) reduces to

$$p = N_v(N_a - N_d) / N_d \times \exp(-E_a / kT). \quad (3)$$

The extrinsic conductivity is obtained from these two expressions for p by setting $\sigma = p e \mu$. Since N_v is dependent on $T^{3/2}$ and since the mobilities are likely to depend on temperature only as a simple power law, the temperature dependence of the conductivity will be dominated by the exponential term in the expression for p . We have for the two cases,

$$\sigma = \text{constant} \times \exp(-E_a/2kT) \quad p \gg N_d \quad (4)$$

$$\sigma = \text{constant} \times \exp(-E_a/kT) \quad p \ll N_d \quad (5)$$

RESISTIVITY - EQUIPMENT

Log R vs 1/T measurements were made using the equipment shown in figure 2. Samples were heated at the rate of about 5° per minute and cooled at the rate of about 1° per minute. Temperatures were measured using a copper-constantan thermocouple in contact with the sample. Resistances were measured with a General Radio electrometer with 9 volts across the sample. The entire heating apparatus was enclosed in an aluminum box for electrical shielding.

RESISTIVITY - RESULTS

Samples were initially of resistance 10^5 - 10^9 ohms. The lowest initial resistances were observed using beryllium oxide substrate and the highest initial resistances were observed using mica substrate. The initial resistance seemed to be a function of the temperature of the anode during the sputtering process - the colder the anode, the lower the initial resistance. It is probable that the highest initial resistances were observed using mica substrate because of

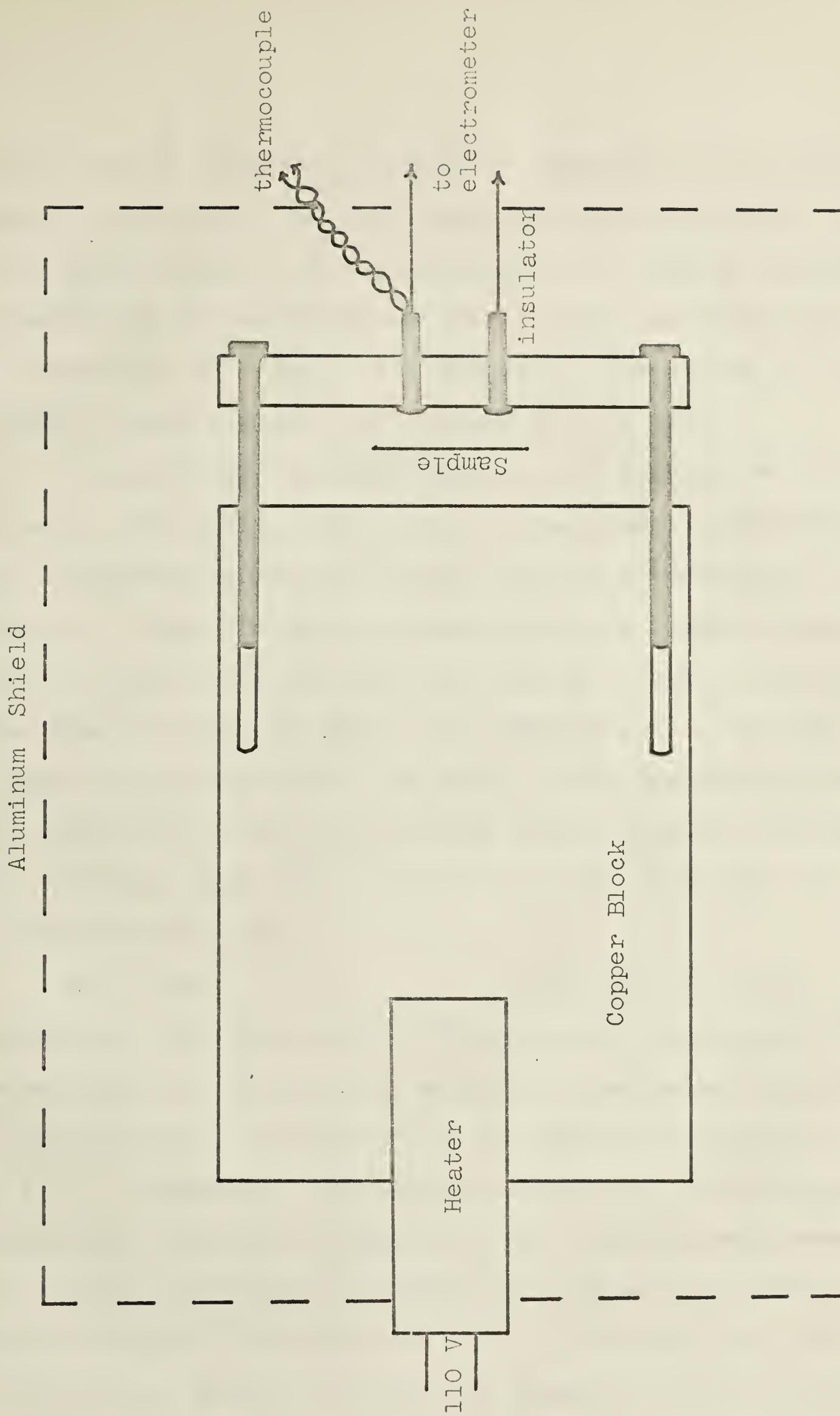


Figure 2 Heater for $\log R$ vs $1/T$ Measurements

poor thermal conduction of mica as compared to beryllium oxide or saphire. The mica substrate was probably not as cold as the anode. The resistance of all samples increased steadily at room temperature over a period of weeks until it was about 10^{11} ohms. The samples of resistance 10^{11} ohms remained fairly stable for periods up to a year.

To calculate the resistivity of the samples, we need to know the thickness. From optical transmission measurements, the thickness can be calculated from the interference fringes. Figure 3 shows the optical transmission of a sample sputtered for two hours at 1500 volts and 6 ma on a saphire substrate. The small fringes are due to the saphire plate, and the large fringes are due to the oxide. The approximate index of refraction of Ag_2O as given by Lange, Handbook of Chemistry, 9th edition, page 1391, is $n = 2.1$.* The thickness t is obtained as follows:

$$m\lambda_1 = 2nt \quad (m + \frac{1}{2})\lambda_2 = 2nt$$

where m is the order of interference and λ_1 and λ_2 are the wavelengths for minimum and maximum transmission, respectively. (See figure 3.) Solving for m , we obtain $m \doteq 11$ which gives $t \doteq 2 \mu$. Therefore, the deposition rate at the conditions stated was about one micron per hour. Similar measurements on a sample deposited on saphire for one hour at 1500 volts and 6 ma gave a thickness of 1.3μ . For estimating the resistivity, we will estimate the deposition rate on mica at

* This value of n may not be correct for our samples, and should be checked by experimentally measuring the sample thickness.

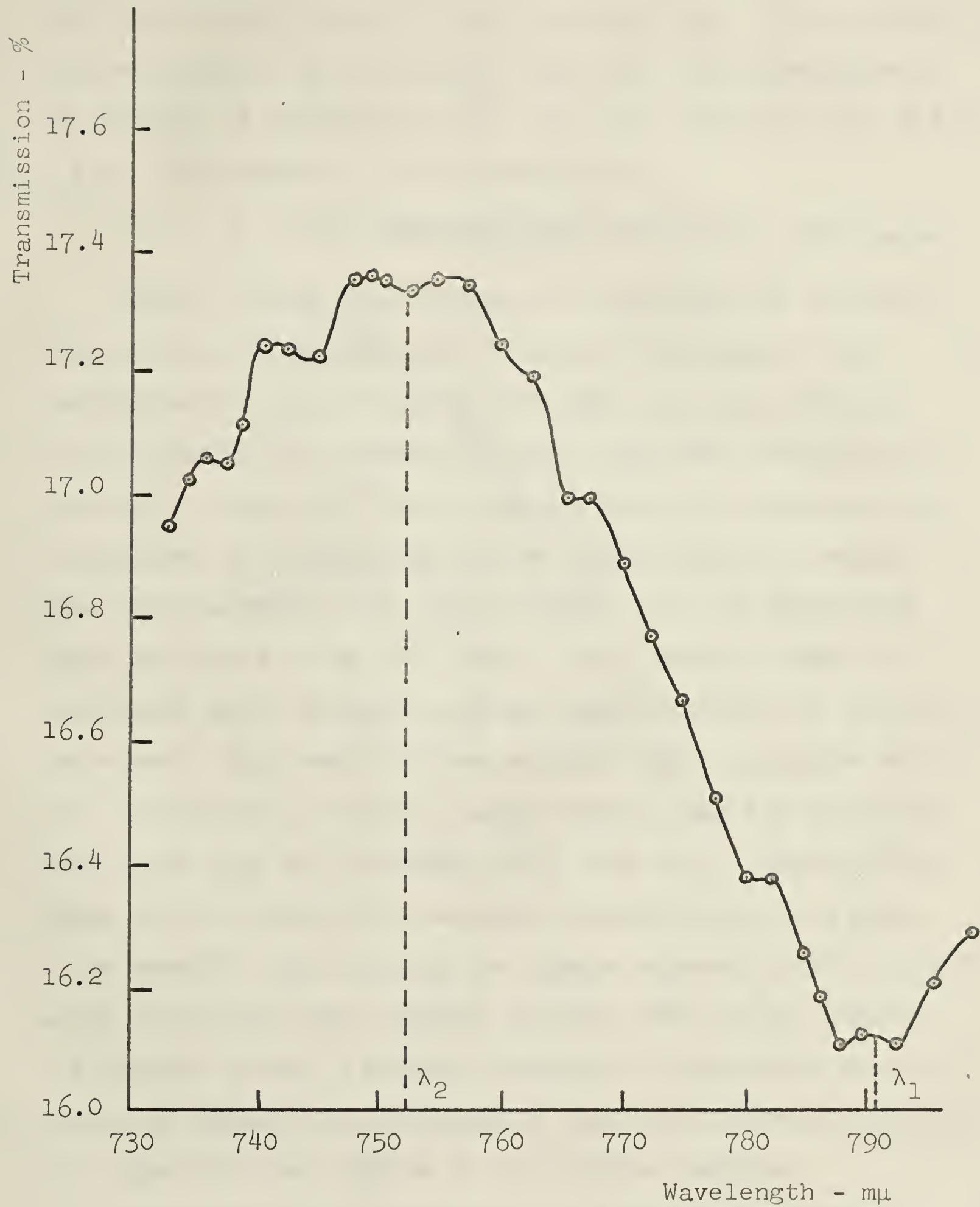


Figure 3 Interference Fringes

1500 volts and 6 ma to be one micron per hour. This should not introduce an error of more than 50%. The dimensions of the samples of resistance 10^{11} ohms were about 0.5 cm x 0.5 cm x 1 μ . This gives for the resistivity:

$$\rho = \frac{10^{11} \text{ ohms} \times 0.5 \text{ cm} \times 10^{-4} \text{ cm}}{0.5 \text{ cm}} = 10^7 \text{ ohm-cm.}$$

Figure 4 shows the increase in resistance of a sample held at room temperature for a period of 50 days. The resistance increased steadily for about 30 days, remained fairly constant for another 20 days, and then dropped quite suddenly to about 10^4 ohms. The decrease in resistance was accompanied by a darkening of the sample along its edges. When the blackened areas were trimmed off, the resistance again was found to be 10^{11} ohms. After several weeks the resistance again dropped, and was again restored by trimming the edges. This behavior was observed only on samples which were originally cut from a larger sample, and the darkening took place only at the edges which were cut. Samples whose edges were not disturbed remained stable for up to a year. It is possible that cutting the sample exposed active surfaces which decomposed more rapidly than the rest of the sample. All samples showed a similar increase in resistance over a period of weeks, but the shape of the curve differed slightly from case to case. Figure 4 is a typical example.

The increase in resistance could be accelerated by heating. Figure 5 shows the effect of heating a freshly pre-

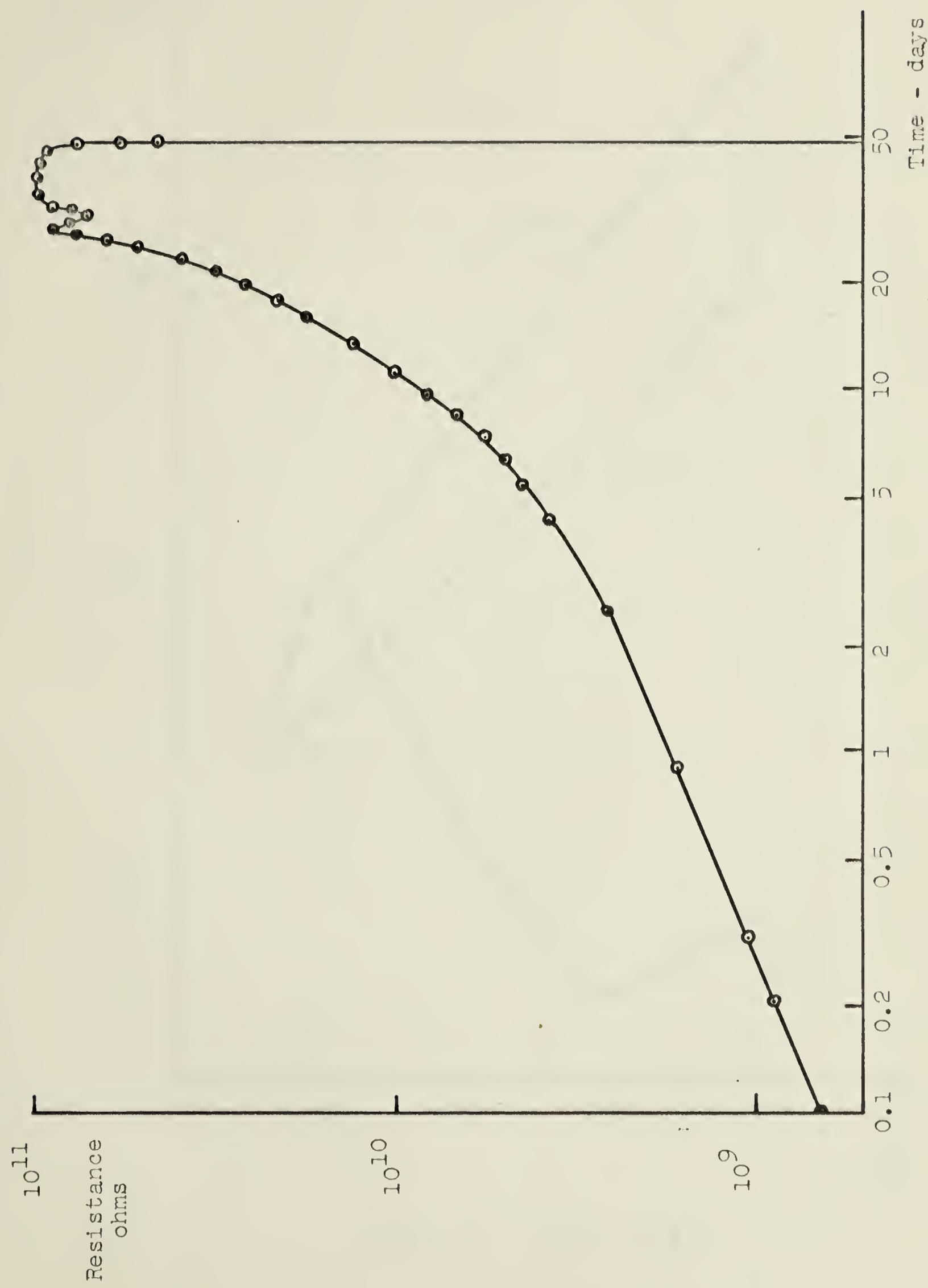


Figure 4 Resistance vs Time

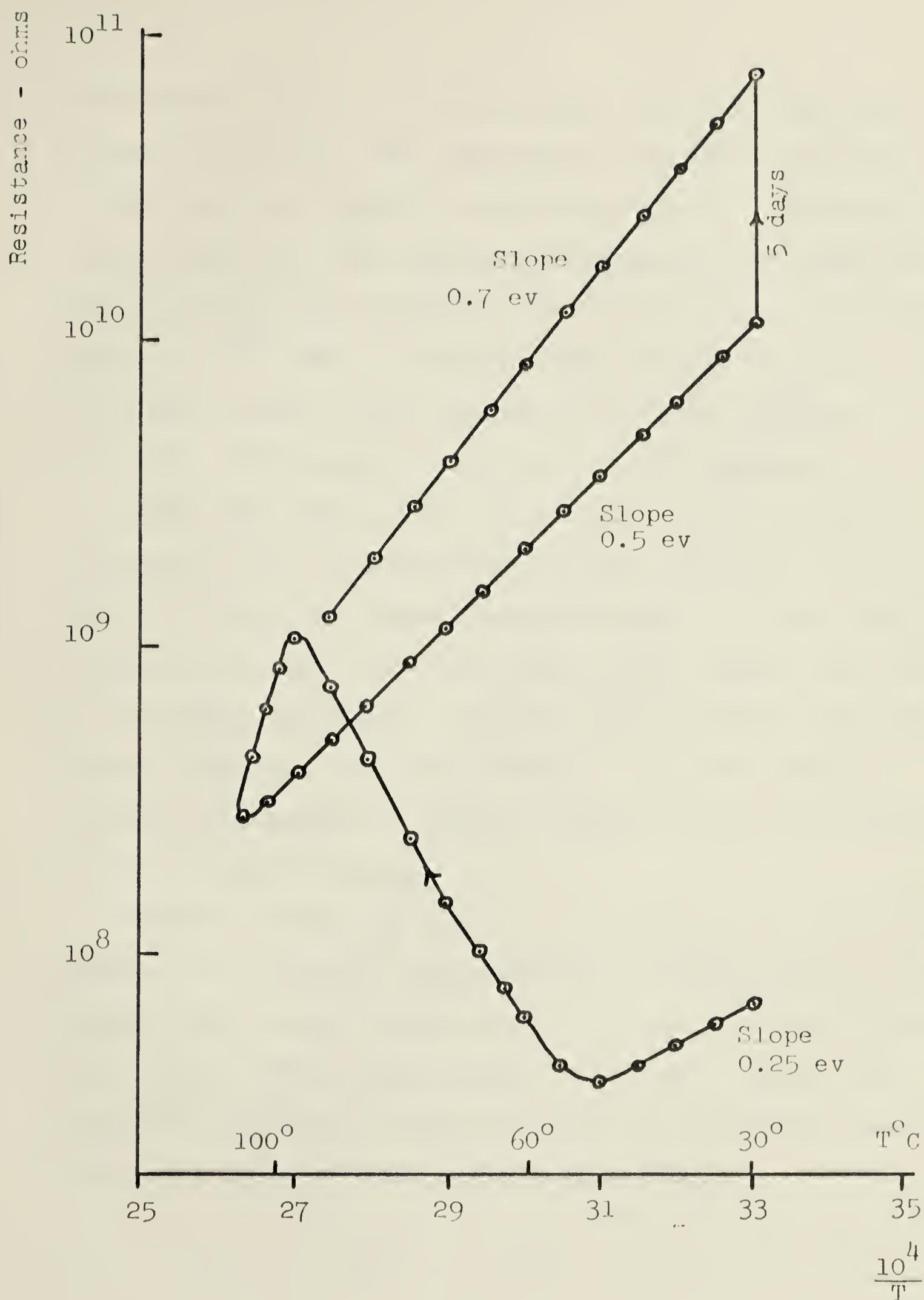


Figure 5 Log R vs 1/T

pared sample in air. The resistance initially decreased with a slope of 0.25 ev. The resistance increased from about 50° to 100° , and then began to decrease again. As the sample was cooled from 100° , the resistance increased with slope 0.5 ev. When the sample had cooled to room temperature, its resistance was about 10^{10} ohms. The sample was held at room temperature for 5 days, and in that time the resistance increased to about 10^{11} ohms. The slope of the $\log R$ vs $1/T$ measurements for the sample was then 0.7 ev. The slope of 0.7 ev and the resistance of 10^{11} ohms remained fairly constant for several weeks, and then the sample darkened along its edges and the resistance dropped. Several samples were heated and cooled in the manner described, and each showed similar characteristics. However, the exact shape of the curve differed slightly from sample to sample. Figure 5 is to be regarded as only a typical example.

Figure 6 shows the $\log R$ vs $1/T$ curves for four different samples. All samples were prepared in approximately the same manner. The slopes obtained are 0.63 ev, 0.67 ev, 0.70 ev and 0.73 ev. The average slope is 0.68 ev. Garner and Reeves⁽¹⁰⁾ obtained a slope of 0.67 ev for similar measurements on samples of chemically prepared Ag_2O .

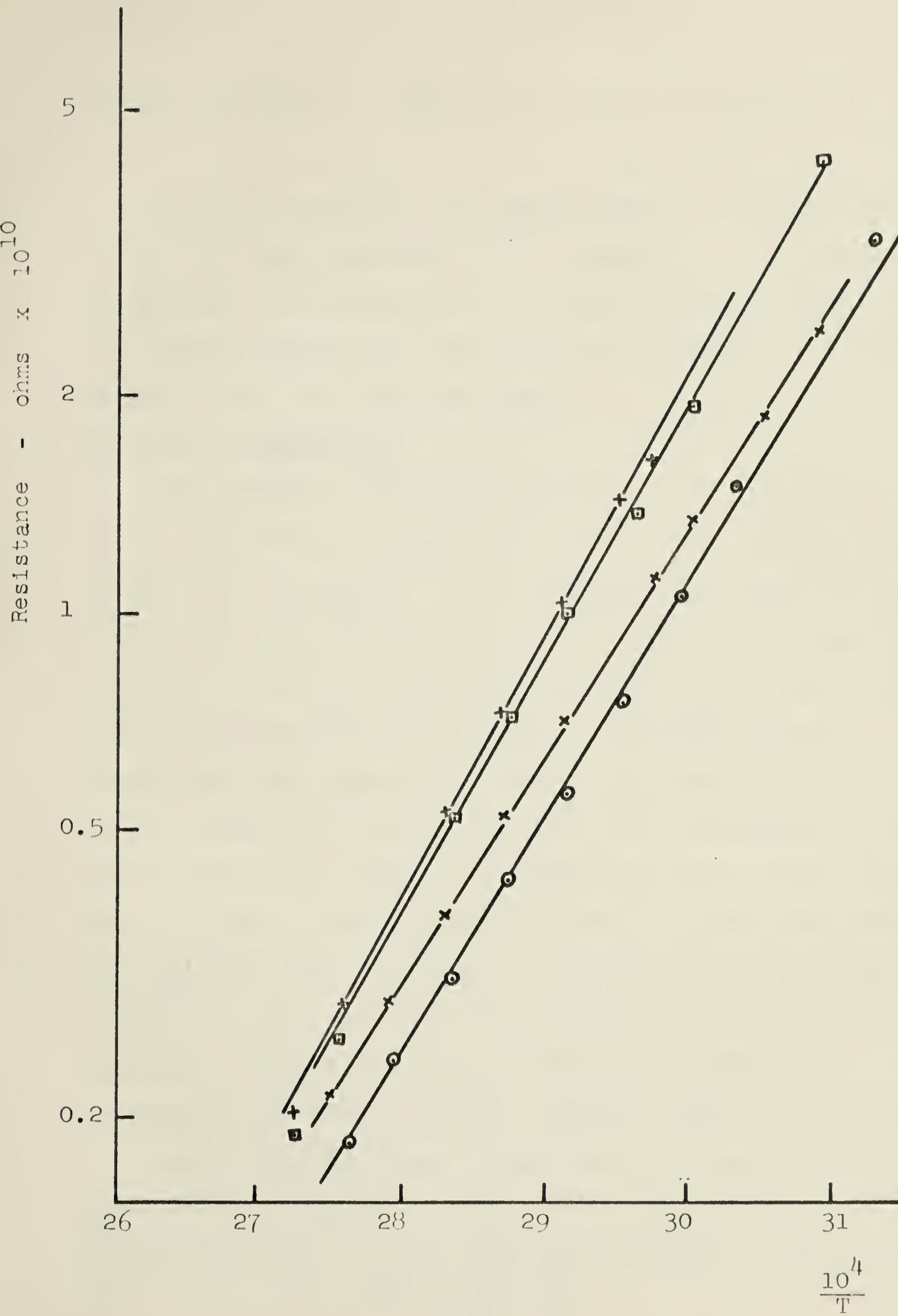


Figure 6 Log R vs 1/T

OPTICAL ABSORPTION - THEORY (See Moss, reference 18)

Optical absorption in a semiconductor may be divided into four types according to the mechanism: (1) intrinsic absorption, (2) absorption involving localized states, (3) carrier absorption, and (4) lattice absorption. We will consider only the first two types.

Intrinsic absorption

By intrinsic absorption we refer to the absorption due to the excitation of valence electrons to the conduction band across the energy gap. It is responsible for semiconductors being opaque and having metallic reflection in the optical region. At sufficiently long wavelengths where the photon energy is insufficient to excite the electrons across the energy gap, the absorption becomes small and the radiation can be transmitted by bulk samples. The wavelength at which this occurs can be used to estimate the width of the energy gap. The band to band absorption spectrum does not have a well defined limit, but falls exponentially for many semiconductors. For materials which show such behavior, it is difficult to specify an unique absorption edge, and yet it is essential to have an unique threshold value of the energy to compare with the unique energy gap which may be determined by the temperature dependence of the conductivity.

According to Fan⁽¹¹⁾, the absorption constant K is given by:

$$K = \pi e^2 F_{if} N(E) / nm$$

where n is the refractive index, m is the electronic mass, F_{if} is a matrix element related to the transition probability, and $N(E)$ is the density of states function. Ideally, $N(E)$ is a discontinuous function, being zero in the case of the conduction band for example when E is below the bottom of the band and finite when E is above it. However, as shown by Parmenter⁽¹²⁾, lattice disorders cause a tailing off of the density of allowed states into the forbidden zone. Moss⁽¹³⁾, suggests that the band edge be defined as the point where $N(E)$ changes most rapidly with E , i.e. where $dN(E)/dE$ is a maximum, and correspondingly to define the 'absorption edge' as the point where the slope of the absorption constant is a maximum, i.e. where $dK/d\lambda$ is a maximum. Experimentally, absorption falls exponentially with energy for energies less than the threshold energy. We will represent the absorption curve by

$$K = K_m \{1 + \exp(\alpha(E_o - E))\}^{-1}$$

where α represents the steepness of the edge, and K_m is the maximum value of the absorption constant K . The definition of 'absorption edge' given above states that $\frac{dK}{dE}$ is a maximum, and hence, $\frac{d^2K}{dE^2} = 0$. This gives $\exp(\alpha(E_o - E_1)) = 1$ at the 'absorption edge' E_1 . Hence, for such a curve the parameter E_o is equivalent to the energy gap, and is determined from the point where the absorption has fallen to half its short wavelength value, i.e. at $K = \frac{1}{2}K_m$.

Localized states

Electrons may be excited to localized states from the valence band, or from localized states into the conduction band. Also, bound electrons or holes may be excited to a higher bound state. Since localized states are associated with energy levels within the energy gap, such excitations usually take place in the infra-red, beyond the intrinsic absorption edge. Ionization energies of the bound states can be estimated from observations of absorption edges corresponding to the states. The value of λ at the absorption edge is estimated as the value of λ at which $d(\log \text{absorption})/d\lambda$ is a maximum.

OPTICAL ABSORPTION - EQUIPMENT

Equipment used for optical absorption measurements is shown in figure 7. The filament from a 12 volt automobile headlight was mounted in an evacuated glass bulb fitted with a NaCl window. Chopped light from this source was focussed on the entrance slit of a Kipp double mirror monochromator with NaCl prisms. Light from the exit slit of the monochromator passed through the sample and was then focussed on a PbS photoconductor. Changes of resistance of the PbS photoconductor caused voltage changes across a resistor. These voltage changes were amplified by a tuned amplifier

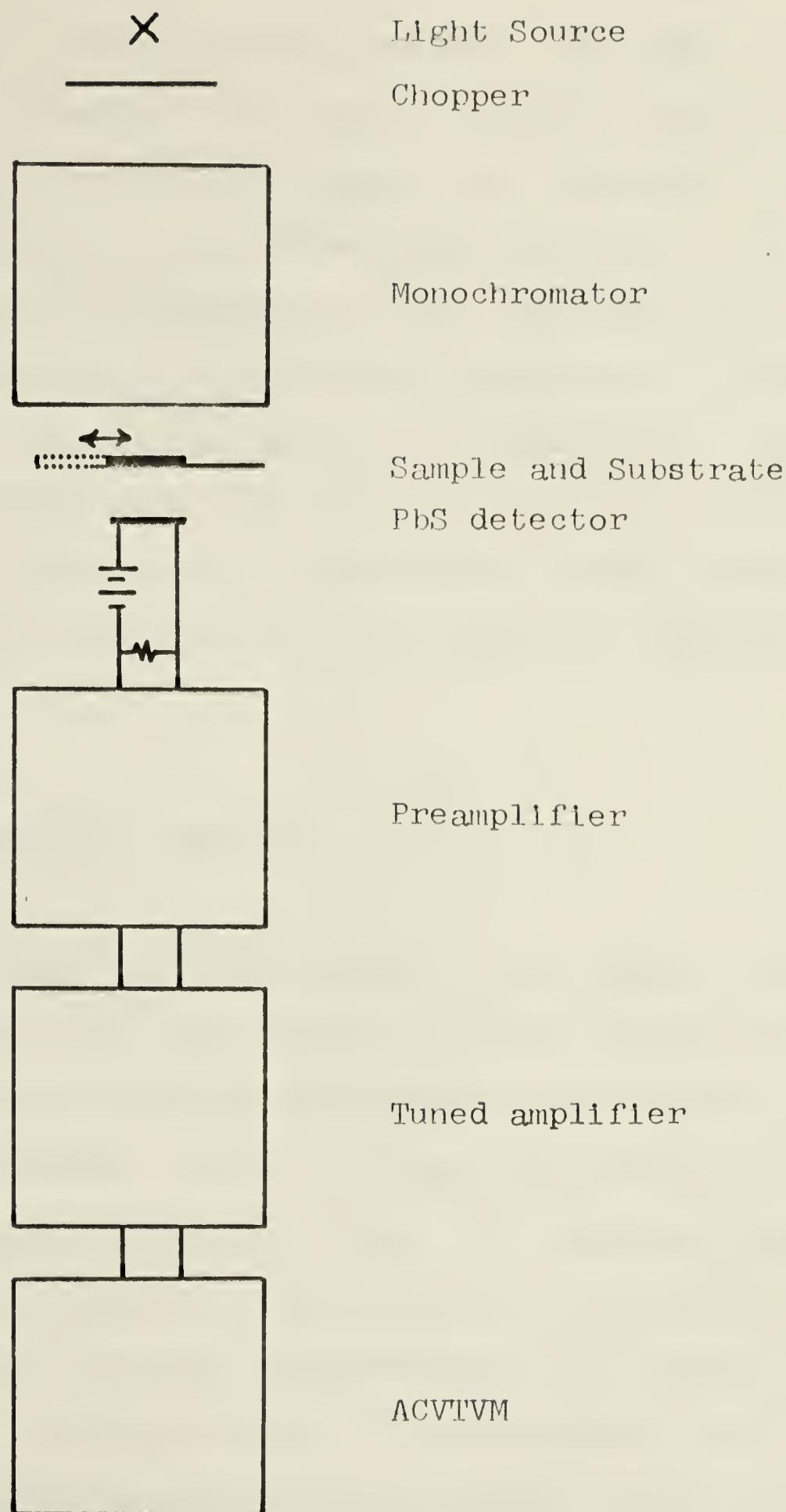


Figure 7 Optical Absorption Equipment

tuned at 38 cps, the chopping frequency, and read on a vacuum tube voltmeter. The light intensity from the monochromator was measured with sample plus substrate in the beam and then with substrate only in the beam, in order to compensate for the absorption of the substrate. The response of the PbS detector was linear with respect to intensity, according to information given by the suppliers. Absorption measurements were made from 1.2μ to 2.8μ , the lower limit imposed by a falling off of the source intensity and the upper limit by a falling off of the detector response.

OPTICAL ABSORPTION - RESULTS

Samples were initially opaque in the visible region. As the samples aged, they became an amber transparent color. Figure 8 shows the optical absorption of two samples of different thickness. Curve (1) shows the absorption of a freshly prepared sample 3μ thick. The absorption edge at about 1.7μ corresponds to an ionization energy of about 0.7 ev. Curve (2) shows the absorption of a freshly prepared sample one micron thick. The absorption edge at about 2.5μ corresponds to an ionization energy of about 0.5 ev. Curves (3) and (4) show the absorption of the same sample after 3 days and after 30 days. As the sample aged, the absorption edge shifted to slightly shorter wavelengths and

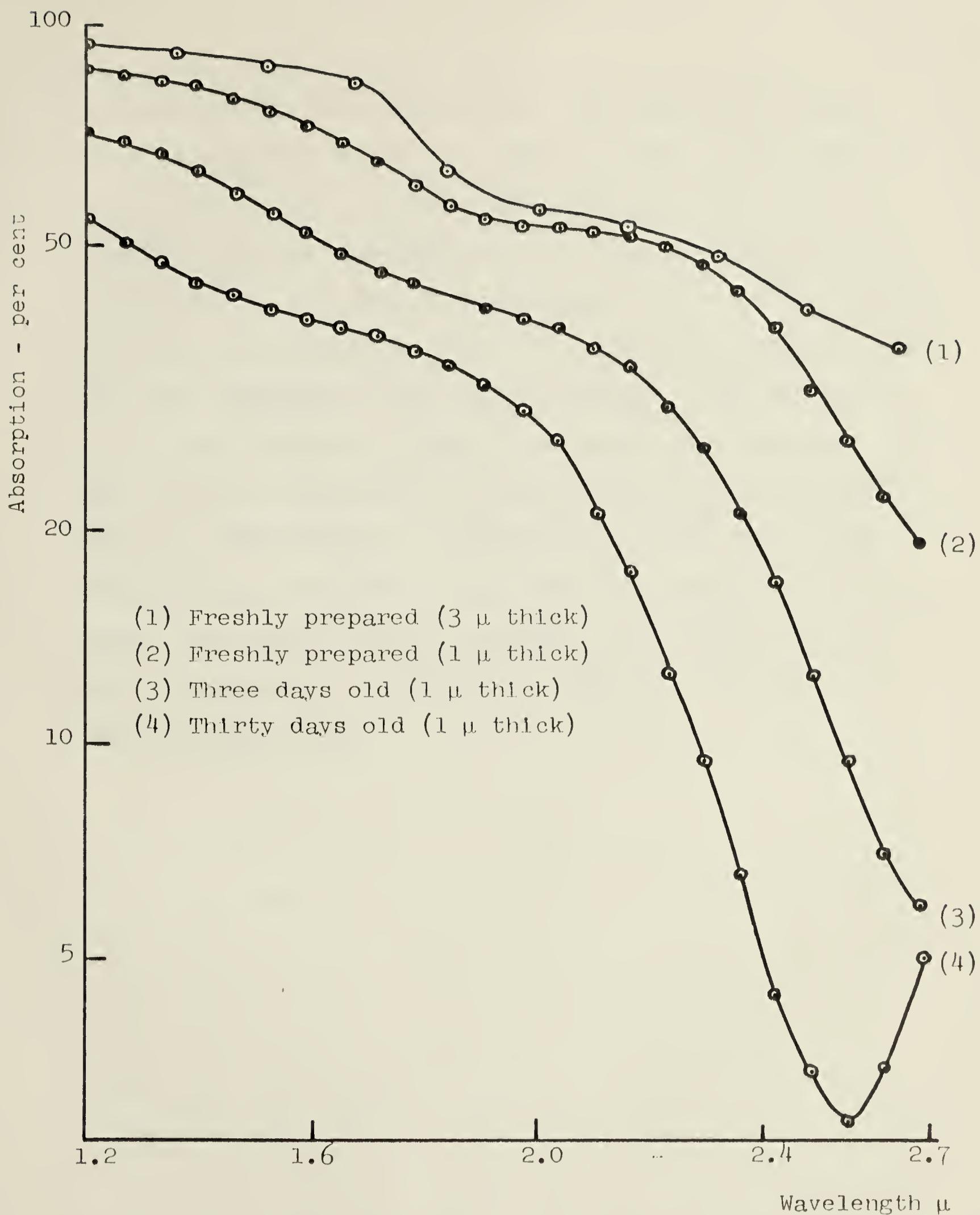


Figure 8 Optical Absorption

to considerably lower absorption. The absorption edge at 2.5μ is not very evident on curve (1), nor is the edge at 1.7μ very evident on curves (2), (3), and (4). It is possible that the absorption at 1.7μ is a property of the bulk material, and thus more important in the thicker sample, and that the absorption at 2.5μ is a surface property, and thus more important in the thinner sample. The absorption of five thin samples and one thick sample was observed. The edge at 2.5μ was present in the spectrum of all five thin samples. The increase in absorption at about 2.6μ (see curve (4)) was observed in all five thin samples as the sample resistance reached a maximum. Not enough data on the thick samples is available to draw any definite conclusions about them.

PHOTOCONDUCTIVITY - THEORY (See Moss, reference 14)

When a semiconductor is illuminated by light of such a wavelength that electrons are raised to the conduction band, the electrons are then free to move through the system under an applied field, and photoconductivity results. If the photoresponse is plotted versus the wavelength, a maximum sensitivity is observed at some value of the wavelength. The sensitivity or photoresponse is defined as $(i_{\text{light}} - i_{\text{dark}})/i_{\text{dark}}$ where i_{light} is the current with the sample illuminated and i_{dark} is the current with the sample not illuminated. For longer wavelengths, the sensitivity decreases exponentially, and for shorter wavelengths, the sensitivity also decreases. The reason for this latter decrease in sensitivity is that the optical absorption increases with decreasing wavelength, so that the photocarriers are produced in a thinner layer as the wavelength decreases. In a thin surface layer the lifetimes of the carriers (defined as the total time the carrier spends in a free state before returning to the valence band in the case of electrons or the conduction band in the case of holes) are reduced because both the high concentration of carriers and the presence of surface imperfections increase the rate of recombination. The sensitivity, which is proportional to the carrier lifetime, is thus reduced. From measurements of the spectral distribution of the photoresponse, it is clear that no absolute threshold wavelength exists, i.e.

there is no wavelength at which the sensitivity vanishes completely. However, thermal measurements give a precise value of activation energy, and it is therefore necessary to define a 'threshold energy' for comparison with this energy. Let us start with the fundamental equation of photoconductivity

$$n = F\tau$$

where n is the number of photocarriers present in the conduction or valence band, F is the number of photocarriers produced per second by the incident light, and τ is the lifetime of a free carrier. A complete discussion of the spectral dependence of the photosensitivity would involve a derivation of the dependence of F and τ on the wavelength. Over a sufficiently narrow wavelength region the lifetimes can be assumed constant. Moss⁽¹⁴⁾ found for such a case that the experimental results could be represented by an expression

$$S(E) = \frac{1}{e^{\beta(E_0 - E)} + 1}$$

where $S(E)$ is the spectral sensitivity, β is a constant, E is the energy at any wavelength, and E_0 is the energy at the 'threshold wavelength'. This expression for $S(E)$ does not contain F or τ explicitly but only the two experimentally determined constants E_0 and β . We will use Moss' expression for $S(E)$, since a detailed discussion of the spectral dependence of F and τ is a problem beyond the scope of this thesis. Moss assumed that the varying sensitivity results from the distribution of levels from which the photoelectrons originate, or

alternately to which they may go. If the distribution is such that there are $N(E)dE$ levels between E and $E + dE$, then with radiation of a given quantum energy E_k the amount of absorption, and hence the sensitivity, will be proportional to the number of centers of energy lower than E_k . The zero of energy is assumed to be at the valence band edge and the distribution of states to be at the conduction band edge. We have

$$S(E) \propto \int_0^{E_k} N(E) dE$$

or $N(E) = G \frac{dS(E)}{dE}$

where G is a constant. By using Moss' expression for $S(E)$ we obtain

$$N(E) = \frac{G e^{\beta(E_o - E)}}{(e^{\beta(E_o - E)} + 1)^2}.$$

Using this distribution of states, Moss then determines the number of electrons which will be in the conduction band due to thermal excitation, which turns out to be $n = \text{constant} \times e^{-E_o/2kT}$, where n is the number of thermally excited electrons. This corresponds to the expression occurring in the conductivity from the simple theory of electrons excited into the conduction band from one definite energy level, namely, $n = n_o \exp(-E_g/2kT)$, where E_g is the energy gap. Hence, by comparison, $E_o = E_g$. When $E = E_g$, $S(E) = \frac{1}{2}$. We reach the important conclusion that the activation energy is determined from the spectral sensitivity curve as the point where the sensitivity has fallen to half value, that is $E_o = E_g = \text{photon energy at } \lambda_{\frac{1}{2}}$.

The dependence of photoresponse on illumination is commonly $I \propto Q^a$, where I is the photocurrent, Q is the incident light intensity, and a lies between 0.5 and 1.0. Consider a semiconductor with M impurity levels per cm^3 near the valence band. The radiation raises Q photoelectrons from the valence band to the conduction band per cm^3 per second. Suppose that originally n' of the acceptor levels are occupied, leaving n' holes in the valence band, and that the conduction band is empty. Let B be the recombination coefficient and n the density of photoelectrons in the conduction band. If the same recombination coefficient is taken for both holes in the valence band and in the acceptor levels, then the equation for build up of signal is:

$$\frac{dn}{dt} = Q - Bn(n+n'+M-n') = Q - Bn(n+M).$$

At equilibrium,

$$\frac{dn}{dt} = 0 = Q - Bn_0(n_0+M)$$

$$n_0(n_0 + M) = Q/B.$$

Hence, for the small signals, with $n_0 \ll M$, the final density of photoelectrons is $n_0 = Q/BM$, i.e. $I \propto Q^{1.0}$. For large signals, with $n_0 \gg M$ (the so-called bimolecular case), the above equation gives $n_0^2 = Q/B$ or $I \propto Q^{0.5}$. Values of a falling between 0.5 and 1.0 are observed for different distributions of states in the forbidden band.

One further concept needed in discussing the results obtained is the concept of response time. We have shown that $\frac{dn}{dt} = Q - Bn(n+M)$. Integrating, we obtain

$$\frac{n_o - n}{n_o + n + M} = \frac{n_o}{n_o + M} \exp\{-B(M + 2n_o)t\}$$

For $n_o \ll M$, $n/n_o = 1 - \exp(-BMt)$, and the response time, defined as the time for the signal to reach $1 - 1/e$ of its maximum value, is $\tau = 1/BM$. For $n_o \gg M$ (the bimolecular case) the situation is considerably more complex and no simple expression can be given for the response time. A study of the build up of signal when the bimolecular recombination process applies has been published by von Hippel and Rittner⁽¹⁵⁾. If there exists in the semiconductor impurity levels which can capture free carriers, and from which the carriers are more likely to be thermally re-excited than to be recombined with a carrier of opposite sign, then the observed response time is greater than that calculated from the simple theory above. These impurity levels, called traps, must be filled or emptied when the light is applied or removed, so observed response times are often many orders of magnitude greater than would be expected from the above discussion. (See Rose, reference 19)

PHOTOCONDUCTIVITY - EQUIPMENT

Equipment used for measurement of the spectral distribution of photoconductivity is shown in figure 9. Light from a 12 volt automobile headlight was chopped at about 0.25 cps, passed through an interference filter, and focussed on the sample. The interference filters were Monopass filters made by Optics Technology Inc. About 10% of the filtered beam was intercepted by a Reeder vacum thermopile with a KBr window. Voltage from the thermopile was measured on an Astrodata microvoltmeter and was proportional to the light intensity, according to the manufacturer. The sample was mounted in a metal shield and connected to a circuit for changing small resistance changes into voltage changes. For convenience, we will call this circuit the VR circuit. Voltage changes from the VR circuit were assumed proportional to the resistance changes of the sample. This assumption will be justified below. Voltages were measured using a General Radio electrometer with input resistance 10^{12} ohms.

To find the approximate error introduced by assuming the resistance change in the sample proportional to the change in output voltage of the VR circuit, an analysis of the circuit is needed. Let the resistors be labeled as in figure 10.

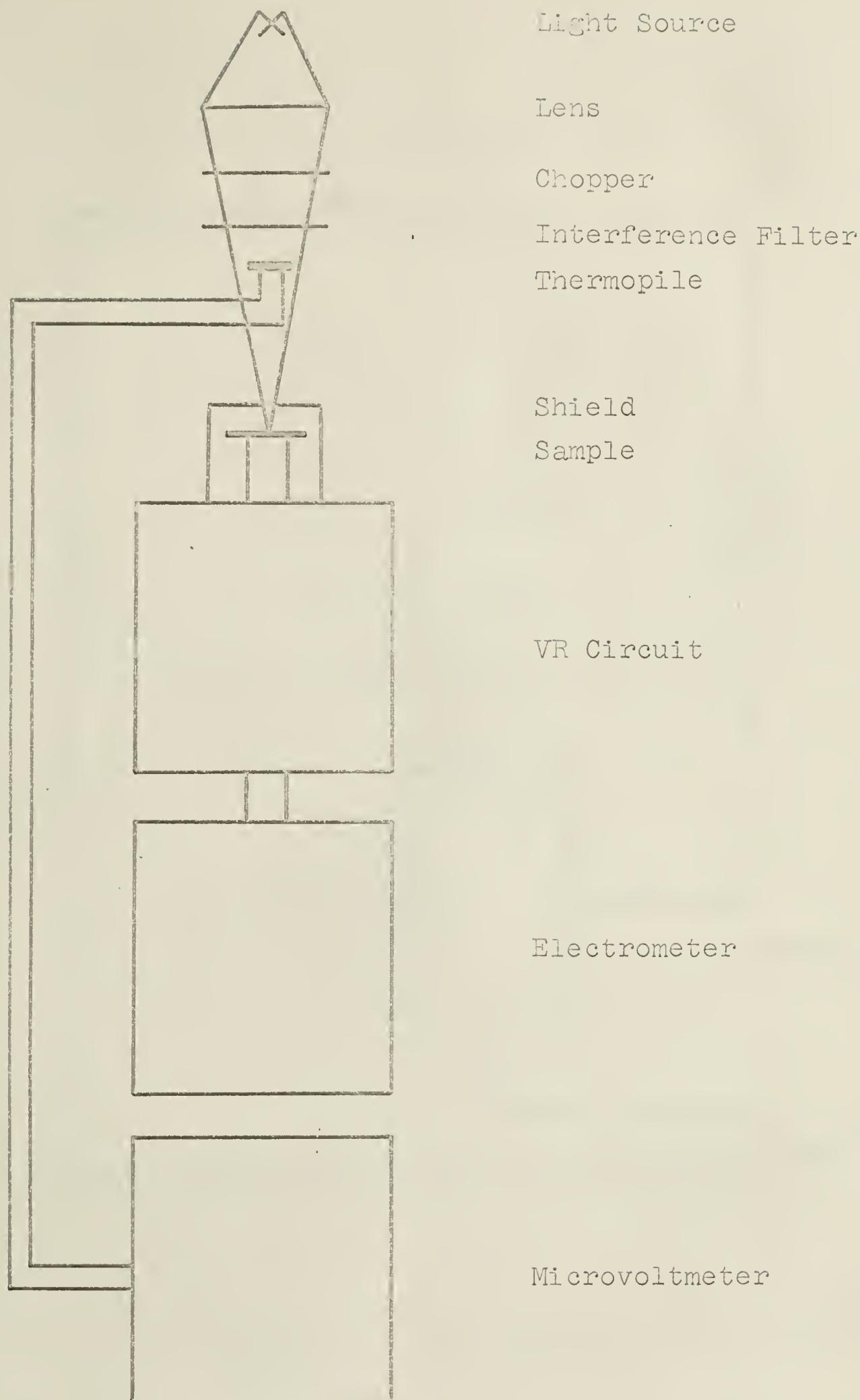


Figure 9 Photoconductivity Equipment

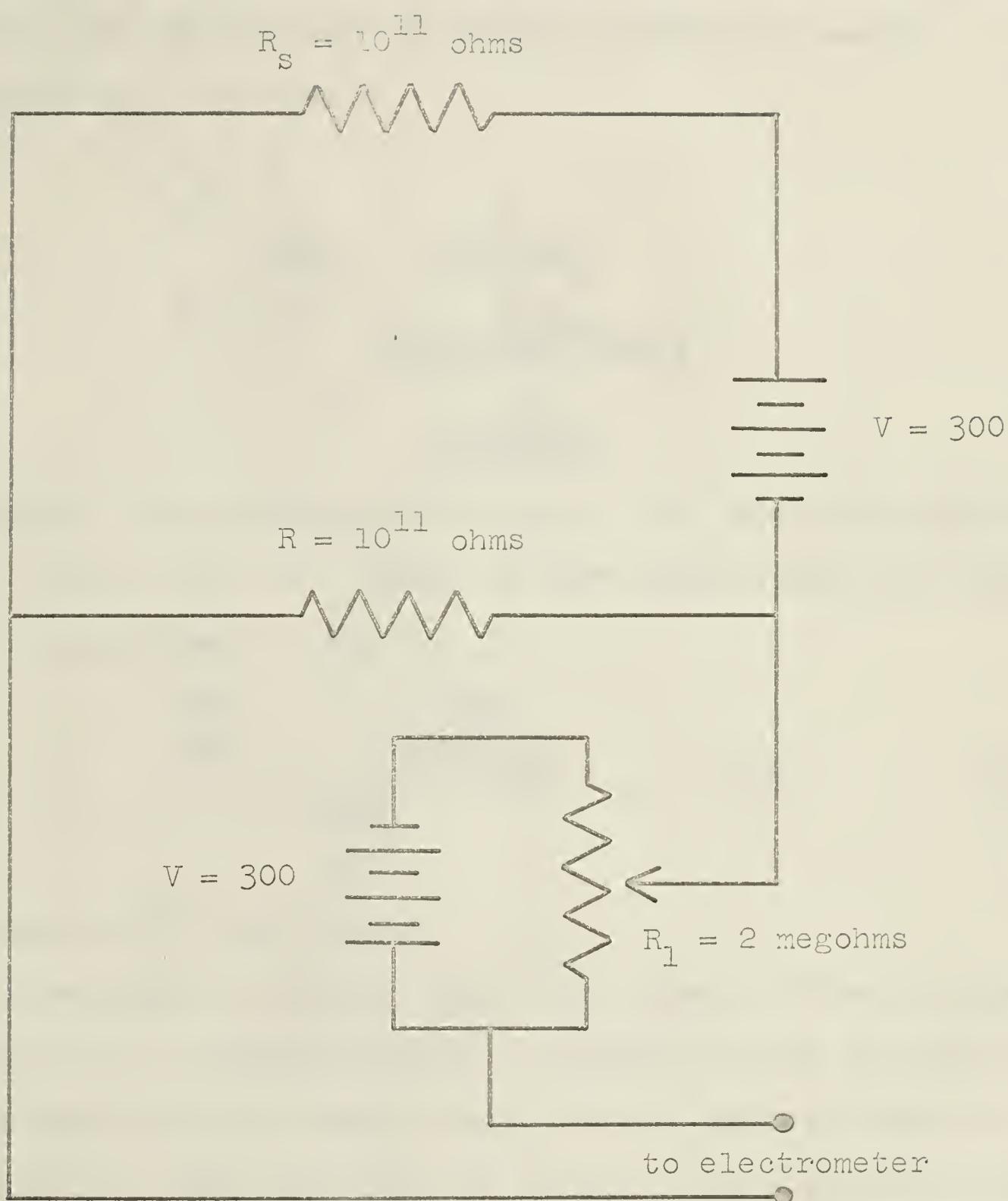


Figure 10 VR Circuit

Let dV be the change of voltage across R and dI be the change of current flowing through R caused by change of sample resistance dR_s . We have

$$R_s \doteq R$$

$$dI = \frac{V}{R+R_s} - \frac{V}{R+R_s+dR_s}$$

$$dV = RdI = \frac{VRdR_s}{(R+R_s)(R+R_s+dR_s)} \\ \doteq \frac{VdR_s}{2(2R+dR_s)}$$

The maximum observed dV was 10 volts. This gives for maximum dR_s the value 1.4×10^{10} ohms. So the maximum error in assuming dV proportional to dR_s is

$$\frac{\frac{VdR_s}{4R} - \frac{VdR_s}{2(2R+dR_s)}}{\frac{VdR_s}{4R}} \times 100\% = 3.3\%$$

This error of 3% was ignored.

The equipment used for measuring response times is shown in figure 11. A pinhole source of light was used so that the light incident on the sample would fall to zero or rise to a maximum in a time much shorter than the time constants being measured. White light was used for the measurements. The waveform was displayed on an oscilloscope and photographed.

The photoresponse vs light intensity measurements were made using the circuit of figure 9. The interference filter peaked at 0.666μ and had a half band width of 150 \AA . Intensity of the light was varied by changing the voltage applied

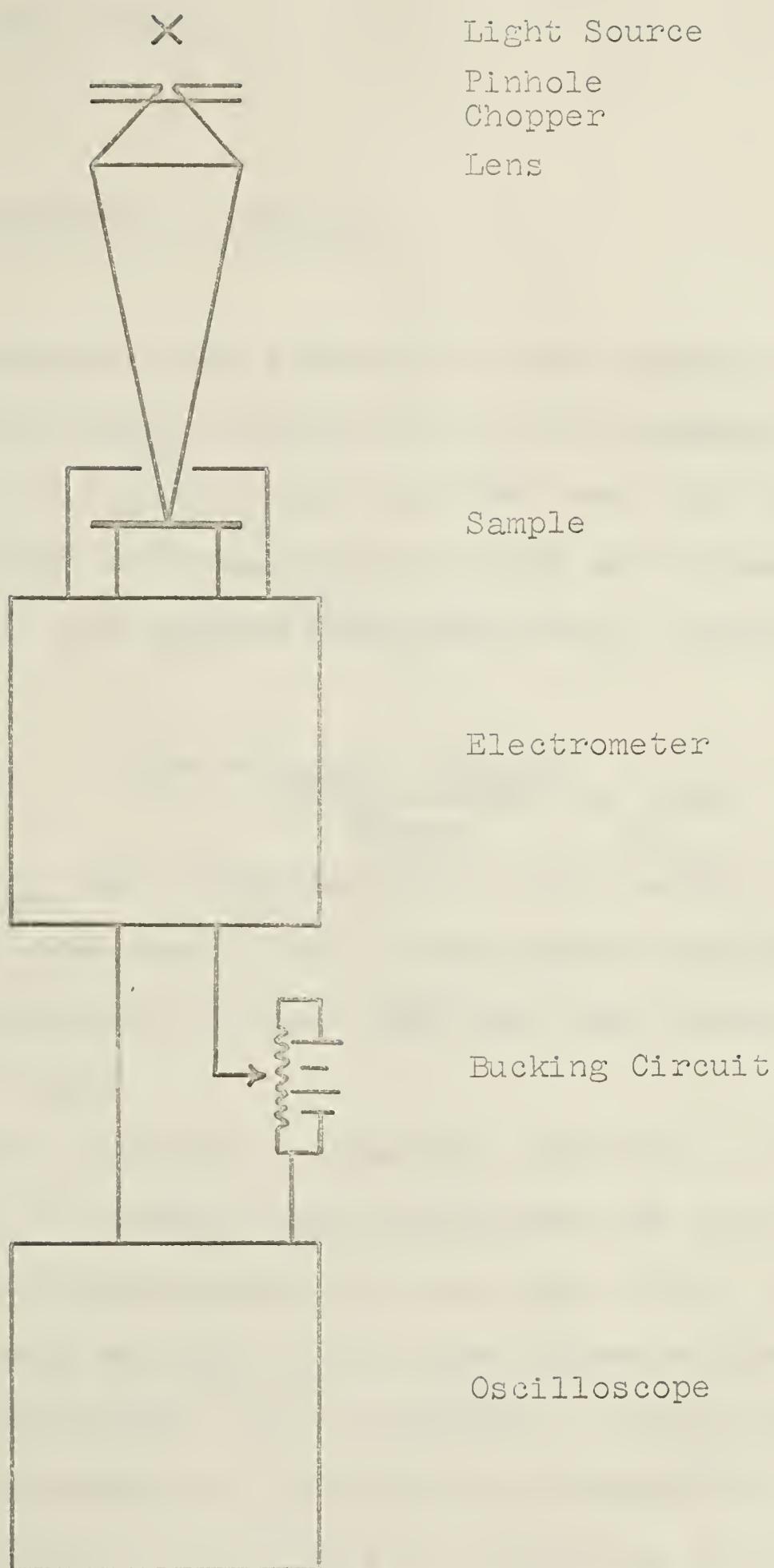


Figure 11. Response Time Equipment

to the light source.

PHOTOCONDUCTIVITY - RESULTS

The samples were initially of low resistance and showed no detectable photoconductivity at room temperature. Photoconductivity could be first detected when the sample resistance reached about 10^9 ohms, and increased as the sample resistance increased. The maximum photoconductivity observed (computed from

$$\% \text{ pc} = \frac{R_{\text{dark}} - R_{\text{light}}}{R_{\text{light}}} \times 100\%$$

where R_{light} was resistance with 5 mw of white light incident on sample) was about 1000%. Most samples reached a maximum photoconductivity of about 500% when their resistance reached about 10^{11} ohms.

Figure 12 shows the spectral distribution of photoconductivity of a sample whose resistance was about 10^{11} ohms and whose % photoconductivity was about 600%. The response showed a peak at about 0.65μ , and decreased for longer and shorter wavelengths, as was expected. The decrease for longer wavelengths is approximately exponential. The value of $\lambda_{\frac{1}{2}}$ is about 0.9μ , giving an energy gap of about 1.4 ev. The source was adjusted before every reading so that the intensity of the incident light was constant for all wave-

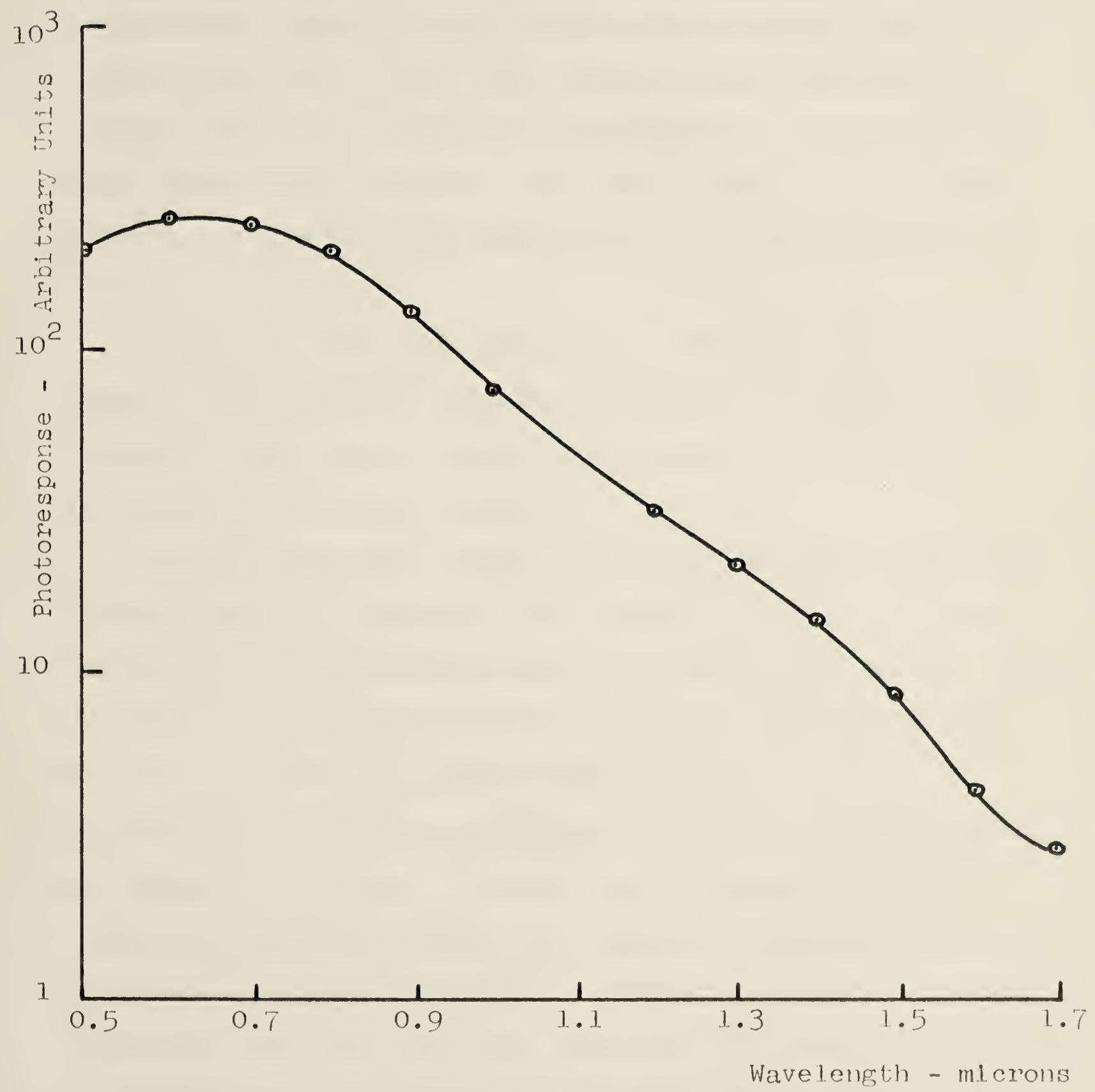


Figure 12 Spectral Distribution of Photoconductivity

lengths. This was necessary because the response vs intensity was not linear. The spectral distribution of four other samples gave similar curves, with energy gaps all lying between 1.4 ev and 1.5 ev. The average energy gap was about 1.43 ev, but not enough data is available to warrant keeping three significant figures. The best we can do is conclude that the energy gap from photoconductivity measurements is about 1.4 ev.

Figure 13 shows the response vs intensity for a typical sample. The slope for high light intensity is about 0.5, as expected. The line of slope 1.0 is drawn for low light intensity, but the fit is poor.

The response time of the sample was estimated using the circuit shown in figure 11. The shape of response vs time curves for several chopper speeds is shown in figure 14. For an order of magnitude estimate of the rise and decay times, the rise and decay was assumed exponential. Since the recombination process was bimolecular in the intensity range of interest, the rise and decay was not exponential, but an order of magnitude estimate was obtained assuming exponential response. From measurements on diagrams such as are shown in figure 14, two rise times and two decay times were estimated. The rise times are 50 msec and 200 msec and the decay times are 50 msec and one second.

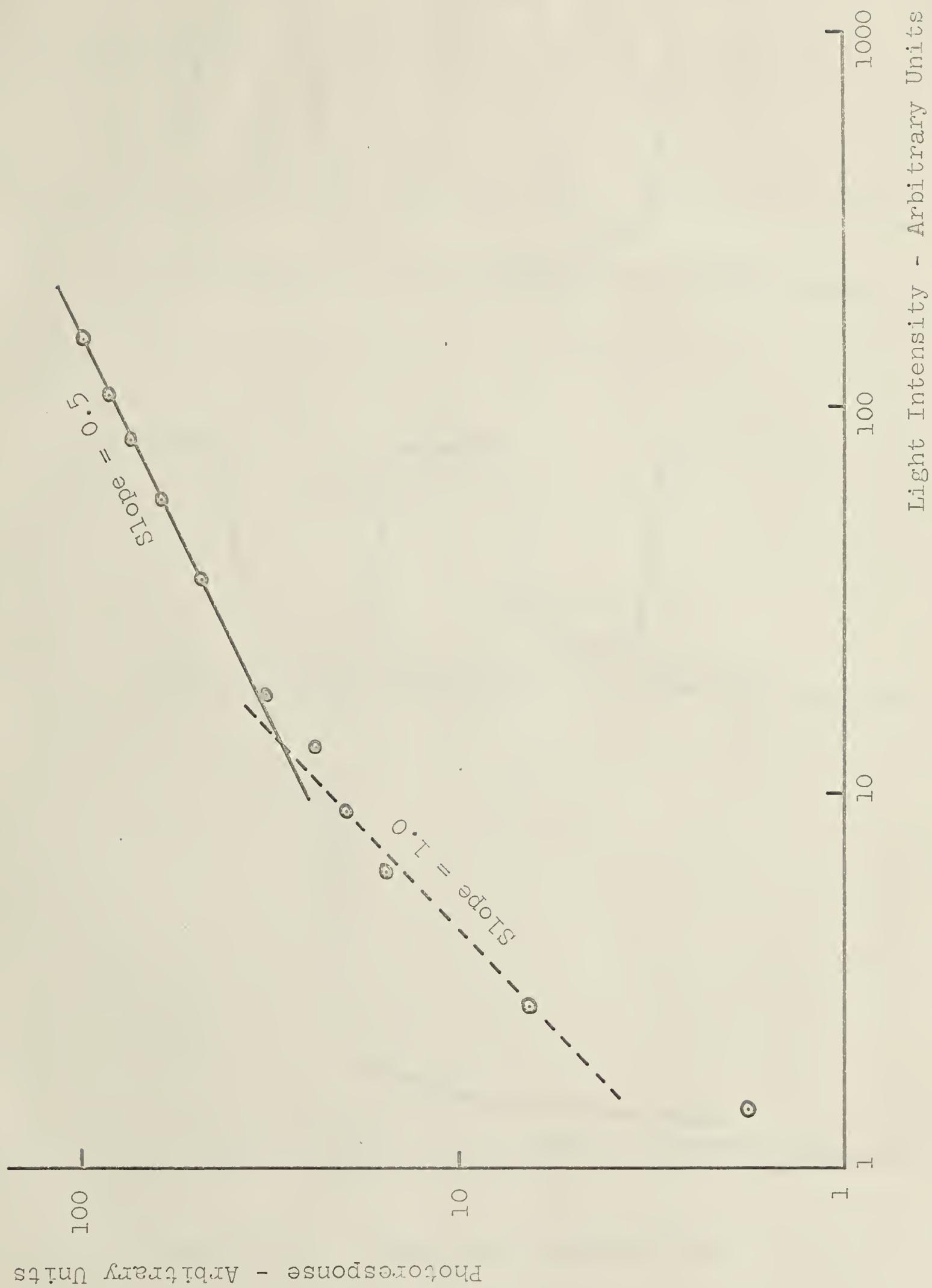


Figure 13 Response vs Intensity

Light Intensity - Arbitrary Units

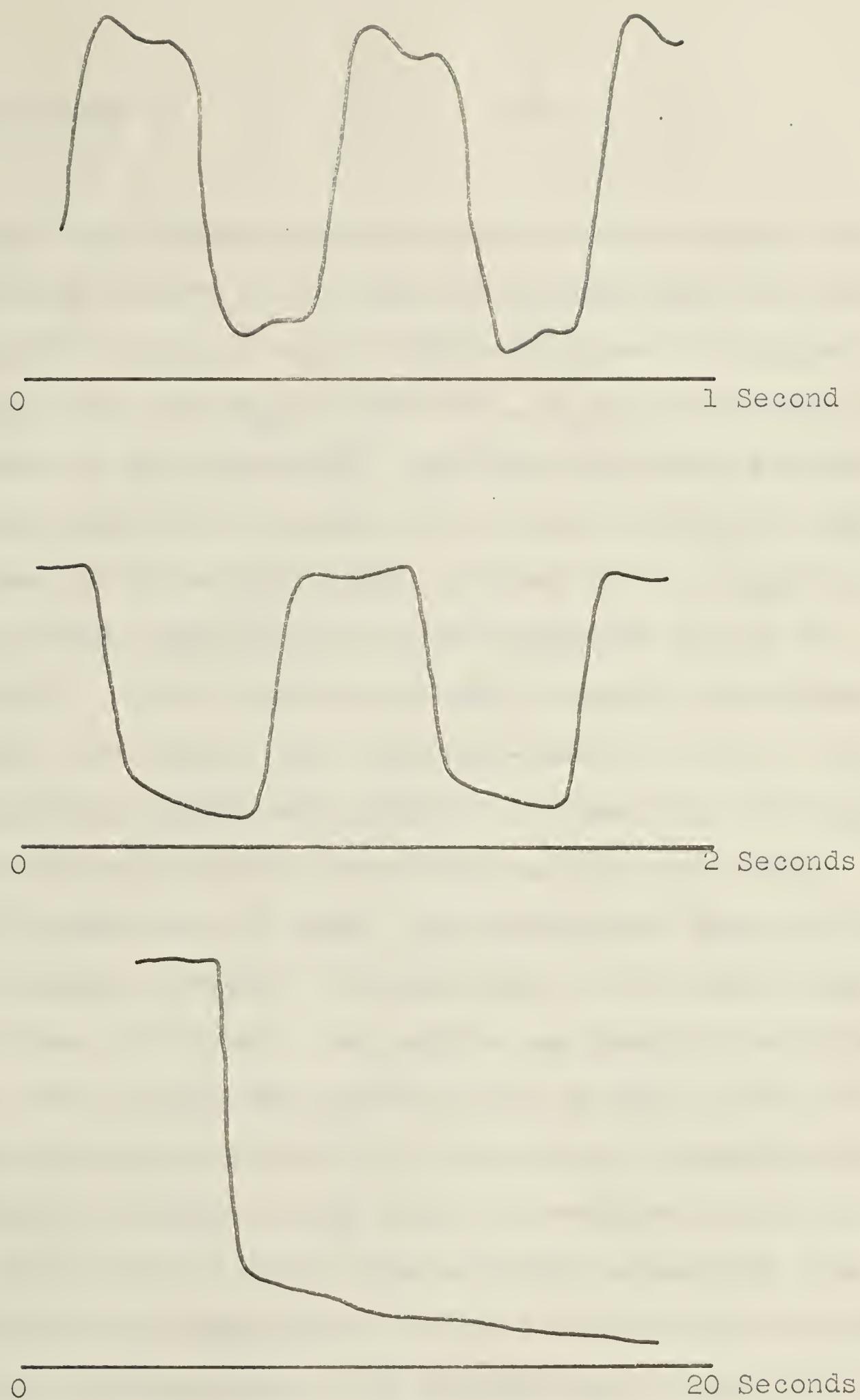


Figure 14 Shape of Response Curves

PROPOSED MODEL

The first problem in proposing a model to explain the experimental results is to identify the material produced. The possible compounds containing only silver and oxygen are Ag_2O_3 , AgO , and Ag_2O . The first, Ag_2O_3 , is unstable and decomposes to AgO on heating. AgO is a greyish-black semiconductor, insoluble in water, but soluble in NH_4OH . AgO decomposes to silver and oxygen at about 100°C . Ag_2O is a brownish-black semiconductor which decomposes in air at about 300°C . It is slightly soluble in water, and soluble in NH_4OH . Our samples were brownish-black in color. The low resistance samples were soluble in water, but the high resistance samples left a very thin residue after being steeped in water for 10 days. The residue was greyish-black and insoluble in NH_4OH . The resistance of the residue was greater than 10^{14} ohms. The residue was possibly colloidal silver. Our samples decomposed in air at about 100°C . In personal correspondence with F.L. Weichman, S. Nikitine stated that single crystals of Ag_2O which he prepared by heating silver crystals in a high pressure oxygen atmosphere were so unstable at room temperature that as yet no reliable measurements have been obtained. The decomposition temperature of 300°C as stated above is for chemically prepared samples. The decomposition of our samples at 100° or lower agrees with the results of Nikitine. A preliminary electron and

X-ray diffraction study indicated that our samples were polycrystalline. However, as yet no correlation between the X-ray diffraction lines obtained from our samples and those obtained from commercial, chemically prepared Ag_2O has been observed. The most solid piece of evidence that we are working with Ag_2O comes from the $\log R$ vs $1/T$ measurements. Garner and Reeves⁽¹⁰⁾, working with three samples of chemically prepared Ag_2O , found an average slope of 0.67 ev from $\log R$ vs $1/T$ measurements. The average slope from four of our samples was 0.68 ev. On the basis of all of the above evidence, we conclude that it is probable that our samples were Ag_2O .

It will be helpful to review the properties of our samples which the model must explain. The initial resistance was relatively low. In time, or as the sample was heated, the resistance increased to a maximum. If the sample was heated above about 100° , the resistance dropped sharply and irreversibly. The slopes of the $\log R$ vs $1/T$ plots were 0.25 ev for a low resistance (10^8 ohms) sample, 0.5 ev for an intermediate resistance (10^{10} ohms) sample, and 0.7 ev for a high (10^{11} ohms) sample. The color of the samples was initially black, and the samples were opaque in the visible region. In time, or as the sample was heated, the color became amber and the samples became transparent. An absorption edge at 0.5 ev shifted from high absorption to low absorption as the color changed from black to amber. Photoconductivity

measurements on the high resistance samples gave an energy gap of about 1.4 ev.

A possible model to explain these properties is shown in figure 15. The sample initially has a density N_a of acceptor states located 9.5 ev from the valence band, and a much smaller density N_d of donor states located at some unspecified position in the forbidden band. The acceptor states are excess oxygen atoms, probably interstitial, and the donor states are oxygen vacancies. The energy gap is 1.4 ev. Initially, the density of excess oxygen is high, so that $p \gg N_d$. This gives (see Resistivity - Theory) $R \propto \exp(E_a/2kT)$ and so $\log R$ vs $1/T$ measurements give a slope of 0.25 ev. The acceptor states account for the absorption edge at 0.5 ev. As the Ag_2O decomposes, it evolves oxygen at a rate dependent upon the temperature, and thus N_a , the density of excess oxygen, decreases with time. The resistance of the sample increases. Since the density of acceptor states is reduced, the absorption edge at 0.5 ev becomes less pronounced. The evolution of oxygen can be accelerated by heating the sample. When the condition $N_d \gg p$ is reached, $R \propto \exp(E_a/kT)$ and $\log R$ vs $1/T$ measurements give a slope of 0.5 ev. When the density of excess oxygen atoms is reduced to approximately the density of oxygen vacancies, the sample behaves much like an intrinsic semiconductor of energy gap 1.4 ev, and $\log R$ vs $1/T$ measurements give a slope of 0.7 ev. Our actual photoconductivity measurements gave a band gap slightly greater

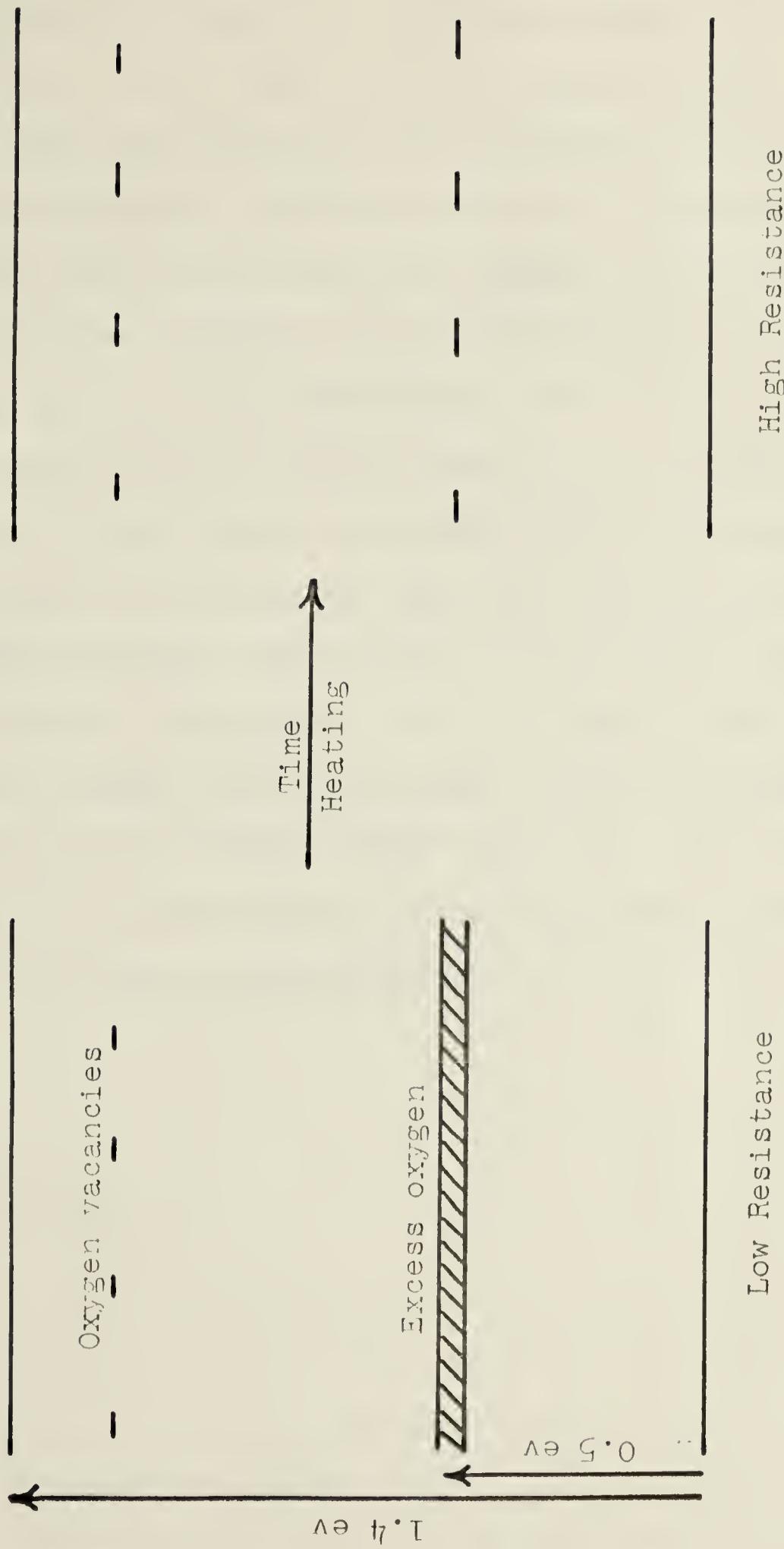


Figure 15 Proposed Model

than 1.4 ev, and $\log R$ vs $1/T$ measurements gave a value slightly less than 1.4 ev. This is to be expected, since Ag_2O is probably polar and there will be a difference in the optical and thermal activation energies due to the Franck-Condon principle. Finally, all excess oxygen is expelled and the density of oxygen vacancies increases as further oxygen is expelled. Nucleation of silver atoms takes place, and the resistance drops. The decomposition of silver oxide is an autocatalytic reaction, with the silver nuclei catalyzing further decomposition. Once silver nuclei are formed, they grow rapidly and the oxide decomposes rapidly. This could account for the sharp drop in the resistance vs time curve. It was observed that samples which had their edges cut with a razor blade decomposed more rapidly than those whose edges had not been cut. It is possible that cutting the sample exposed active surfaces on which nucleation of silver atoms was accelerated.

CONCLUSION

A method of producing thin films of silver oxide by cathodic sputtering of silver in an oxygen atmosphere onto a cooled substrate was developed. The temperature dependence of the conductivity of these films and of chemically prepared Ag_2O was the same. The thin films were probably Ag_2O . X-ray and electron diffraction studies indicated that the samples were polycrystalline rather than amorphous. The samples were initially of low resistance and opaque in the visible region. In a period of time which could be shortened by heating the samples, they became an amber transparent color and the resistance increased. These high resistance samples were relatively stable, but after a time their resistance dropped sharply. The resistivity of these samples reached a maximum of 10^7 ohm-cm. The variation of resistance with temperature between 30°C and 100°C indicated a band gap of 1.4 ev and an impurity level 0.5 ev from a band edge. The photoresponse for wavelengths between 500 μm and 1.7 μ indicated an energy gap of 1.4 ev. Photoresponse was found to vary with the square root of the intensity for high light intensities. Mechanisms of decomposition and a band scheme were proposed which accounted for the observed properties. A set of acceptor states (excess oxygen) 0.5 ev from the valence band slowly disappeared as the sample evolved oxygen. The stable, high resistance samples were samples which had expelled all excess oxygen. The final resistance drop was caused by nucleation of silver atoms causing the catalytic decomposition of

the oxide.

Studies which need to be done in the future are:

- (1) Confirmation of sample composition by X-ray and electron diffraction studies.
- (2) Measurement of crystallite size and observation of influence of sputtering conditions and substrate conditions on crystallite size.
- (3) Study of optical absorption at low temperatures, and identification of exciton structure if present.
- (4) Study of decay mechanisms by observation of rate of evolvement of oxygen, and rate of absorption and nature of absorbed and chemisorbed gases.
- (5) Study of entire infra-red absorption spectrum, and comparison to Cu_2O spectrum.
- (6) Study of effect of sample thickness on sample properties.
- (7) Study of photoconductivity of initial low resistance samples at low temperatures.
- (8) Study of possibility of producing single crystals of Ag_2O by depositing epitaxially on Cu_2O .

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